Synthesis of an acidic biomorphic carbon-based catalyst for simultaneous esterification and transesterification reactions

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The activation of cellulose followed by sulfonation produces a biomorphic functionalized carbon material with acid catalytic activity as a solid-acid replacement for homogeneous catalysts. The carbon-based material contains carboxylic and sulfonic acid groups and exhibits high catalytic performance for liquid-phase acid-catalyzed reactions in presence of water. The activation of cellulose at high temperature (600ºC) followed by sulfonation also results in an amorphous carbon with an acidity value close to 1.52 mmol.g^{-1}. The catalytic test shows that the sulfated carbon has enough amount of sulfonic acid groups and exhibit high catalytic activity and stability for esterification and tranesterification of raw materials; achieving a comversion value close to 90.5% at 2h of reaction comparable to an homogeneous catalysts. Structural and active site analyses suggest that the marked difference in catalytic activity is due to the accessibility of reactants to sulfonic acid groups in the carbon structure.

1. Scope

In this study, a pyrolysis method using methane sulfonic acid was employed to sulfonate biomorphic carbon to prepare solid acid catalysts. The functionalized carbon was characterized by conventional techniques (XPS, CNHOS, Raman and FTIR). The reactivity of these catalysts were evaluated with respect to their performance in catalyzing the simultaneous esterification and transesterification to produce biodiesel from oleins.

2. Results and discussion

Structured biomorphic carbon based-catalysts (Figure 1) was prepared by cellulose pyrolysis and was then was treated with oxidizing agent, HNO_3, to develop surface oxygen complexes and then functionalized by impregnation using methanesulfonic acid solution as sulfonating agent. After impregnation step, this catalyst was activated under a nitrogen atmosphere at 300ºC for 2h and a heating rate of 10ºC. min^{-1}. XPS data are showed in Table 1. The non-functionalized support displays a smaller O/C ratio (0.06) while the support treated with HNO_3 show a higher O/C ratio close to 0.21; increasing up to 0.50 for functionalized SO_3H-C catalyst. C_{1s} region deconvolution shows binding energies of ~284.6 eV and ~286.1 eV corresponding to C-C/C=C and C-O-C corresponding to C-graphitic and phenolic-ether species. O_{1s} signal reveals *C=O* double bonds (531.4 eV) and C–O single bonds (533.4 eV). S_{2p} region was also analyzed fitting in one signal at 169 eV which is assigned to the higher oxidation state (+6) of sulfur in SO_3H groups. When HNO_3 and MSA was used for oxidation and sulfonation, the material exhibits an easily observable modification in the surface distribution.

Table 1. XPS data

	Relative amount (%)				Atomic ratio	Deconvolution of C_{1s} O_{1s} and S_{2p}		
	C_{1s}	O_{1s}	N_{1s}	S_{2p}	O/C	C_{1s}	O_{1s}	S_{2p}
C support [a]	94.78	5.22	-	-	0.06	284.8 (77.5) 286.41 (22.45)	532.9 (97.05) 535.6 (2.95)	-
C support [b]	80.00	17.10	2.82	-	0.21	284.61 (79.94) 286.11 (20.06)	532.57 (94.62) 534.53 (5.38)	-
SO_3H_C	62.42	30.55	1.39	5.65	0.50	284.40 (90.11) 286.12 (9.89)	531.77 (63.66) 533.20 (36.34)	169.5 (100)

[a] non-functionalized support [b] functionalized support

The acid site density was 1.52 mmol.g^{-1}. Simultaneous esterification and transesterification of fatty acid (model FFAs and oleins=FFA+glyceric species) with methanol was used to verify the catalytic activities of the sulfonated carbon catalysts. The catalyst activity of sulfuric acid and MSA was also tested for comparison. **Fig. 1** depicted the increase in yield percentage of biodiesel with increasing the time of reaction compared with homogeneous catalysts for short times as sulfuric acid and MSA catalyst. Homogeneous esterification were also performed to determine the reaction activity under similar conditions for compared with sulfonated carbon catalysts. The activity of homogeneous catalysts as H_2SO_4 and MSA was the greatest due to its inherent higher concentration of acid sites at short time of reaction with yields to biodiesel close to 97 and 99 %, respectively. The yields to FAME using sulfonated carbon as a catalysts are above 84.9% under the same conditions of homogeneous reaction.

Figure 1. Image of the structured biomorphic sulfonated carbon based-catalyst

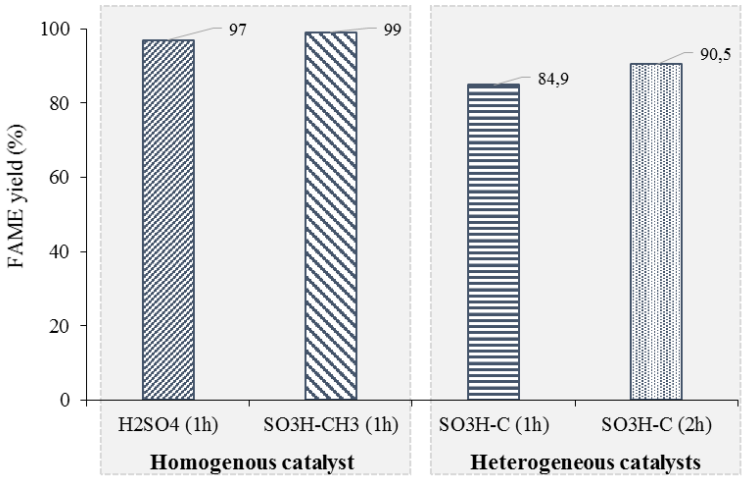

Figure 2. Catalytic activity of sulfonated carbon: 12:1=MeOH:Oil; 120ºC; 10.34 bar; 3 wt% catalysts.

3. Conclusions

The biomass–based sulfonic-functionalized solid material -as a hydrophobic material, it can prevent the hydration to maintain the stability of the acid strength- appears as an active solid acid catalyst in the simultaneous esterification and transesterification of oil with methanol to produce biodiesel. Notably, the biomorphic carbon bearing $–SO_3H$ groups facilitate the accessibility of bulky high fatty acid substrate molecule, yielding the high biodiesel percentage under mild reaction conditions as well. In addition, the functional –COOH group generated during the activation and sulfonation probably contribute to the catalytic activity of the synthesized solid despite of its weak initial acidity.

References

1. A. Boyano, C. Herrera, M.A. Larrubia, L.J. Alemany, R. Moliner, M.J. Lázaro, Chem. Eng. J. 160 (2010) 623–633.